

New wave-number calibration tables for H₂O, CO₂, and OCS lines between 500 and 900 cm⁻¹

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The pure rotational lines of H₂O, the ν_2 band of CO₂, and the ν_1 band of OCS were simultaneously recorded by a Fourier transform spectrometer. The resolution achieved was ~ 0.0045 cm⁻¹, and the precision of the line position was typically 3.6×10^{-5} cm⁻¹ or 1.2 MHz (standard deviation). The spectrum improves the accuracy of wave numbers of calibration lines in the region between 500 and 720 cm⁻¹ by a factor of ~ 10 .

I. Introduction

The main purpose of this work was to transport the high accuracy of seven OCS lines¹ in the ν_1 band to pure rotational lines² of H₂O and the ν_2 band³ of CO₂ at lower wave numbers. These OCS lines were very suitable for this purpose because they are strong enough, and there are no strong bands of OCS between 550 and 720 cm⁻¹ overlapping H₂O and CO₂ lines. Another possibility is to use more accurate lines^{4,5} of the hot band of ¹²CO₂ or ¹³CO₂ as a reference spectrum. However, the intensities of these hot-band lines are small, and we have to employ such a high sample pressure that the ν_2 lines of ¹²CO₂ or ¹³CO₂ are saturated and overlap the H₂O lines in this region. The best condition is achieved when the absorption of the lines under study is nearly equal to that of the reference lines.

Water lines are the most important for us, because in the future all our Fourier transform spectra will be calibrated against H₂O lines. The reason for this is that water lines are spread over a wide wave-number range, and the line density is low and hence suitable for interferometric measurements. On the other hand, the wave-number table of the ν_2 band of CO₂ helps, we hope, in the calibration of tunable diode lasers.

II. Experimental

A. Instrument

The standard spectrum was recorded on a Fourier transform spectrometer⁶⁻⁸ at the University of Oulu. The instrument is presently working with a resolution of ~ 0.0045 cm⁻¹ and a very high wave-number precision of about $\pm 4 \times 10^{-5}$ cm⁻¹ or 1.3 MHz (standard deviation) below 1200 cm⁻¹. The latest modification of this instrument is a dynamic alignment system⁹ of the interferometer. The tilt-free movement of the mirror in the interferometer was accomplished by measuring the optical path difference for three points 10 mm apart on the surface of the moving mirror. The phase detectors between the laser fringes at these three points produce feedback signals for the servo system of the alignment.

B. Spectra

The spectra were recorded under the following conditions: the absorption path length was ~ 1 m, and the partial pressures of H₂O, CO₂, and OCS were 1.9, 0.05, and 0.30 Torr, respectively. Mylar, 2 μ m in thickness, was used as a beam splitter, and the detector was a Golay cell with diamond windows. The KBr windows were used on the gas cell, and an extra optical filter (OCLI) was used with the 500–1200-cm⁻¹ range.

III. Results

A. ν_1 Band of ¹⁶O¹²C³²S

The wave-number scale of the recorded spectrum was fixed with the help of seven OCS lines measured by a heterodyne frequency technique.¹ The observed and calculated wave numbers of the lines in the ν_1 band of OCS are given in Table I. The standard deviation in the fit to a fourth-order polynomial was 3.6×10^{-5} cm⁻¹. Our calculated values are in good agreement with the

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Table I. Observed and Calculated Wave Numbers of the Fundamental $10^0 \leftarrow 00^0$ of $^{16}\text{O}^{12}\text{C}^{32}\text{S}$. Lines Marked with A are Blended, and They Have Not Been Used in the Calculations

0	-	-	-	859.37144	.37133	-11	0
1	858.56122	.56125	3	859.77473	.77489	16 A	1
2	858.15430	.15426	-4	860.17681	.17676	-5	2
3	857.74617	.74614	-3	860.57768	.57773	5	3
4	857.33683	.33684	1	860.97733	.97730	-3	4
5	856.92629	.92630	1	861.37577	.37575	-2	5
6	856.51454	.51451	-3	861.77299	.77300	1	6
7	856.10159	.10159	0	862.16899	.16902	3	7
8	855.68744	.68744	0	862.56378	.56386	8	8
9	855.27208	.27206	-2	862.95734	.95720	-14 A	9
10	854.85551	.85514	-37 A	863.34968	.34969	1	10
11	854.43776	.43776	0	863.74080	.74079	-1	11
12	854.01881	.01876	-5	864.13070	.13066	-4	12
13	853.59865	.59865	0	864.51937	.51937	0	13
14	853.17729	.17729	0	864.90681	.90677	-4	14
15	852.75474	.75472	-2	865.29303	.29302	-1	15
16	852.33099	.33099	0	865.67801	.67801	0	16
17	851.90605	.90603	-2	866.06176	.06175	-1	17
18	851.47991	.47991	0	866.44429	.44423	-6	18
19	851.05257	.05258	1	866.82558	.82565	7	19
20	850.62404	.62405	1	867.20563	.20563	0	20
21	850.19432	.19437	5	867.58444	.58442	-2	21
22	849.76341	.76339	-2	867.96202	.96202	0	22
23	849.33130	.33130	0	868.33836	.33838	2	23
24	848.89800	.89802	2	868.71346	.71348	2	24
25	848.46352	.46359	7	869.08731	.08732	1	25
26	848.02784	.02789	5	869.45992	.45996	4	26
27	847.59097	.59097	0	869.83128	.83122	-6	27
28	847.15291	.15294	3	870.20140	.20140	0	28
29	846.71366	.71366	0	870.57026	.57029	3	29
30	846.27323	.27327	4	870.93787	.93792	5	30
31	845.83161	.83118	-43 A	871.30424	.30420	-4	31
32	845.38880	.38875	-5	871.66934	.66939	5	32
33	844.94480	.94483	3	872.03319	.03317	-2	33
34	844.49961	.49959	-2	872.39578	.39582	4	34
35	844.05324	.05325	1	872.75712	.75711	-1	35
36	843.60568	.60569	1	873.11719	.11720	1	36
37	843.15694	.15695	1	873.47599	.47596	-3	37
38	842.70701	.70701	0	873.83353	.83356	3	38
39	842.25589	.25592	3	874.18980	.18981	1	39
40	841.80359	.80363	4	874.54481	.54484	3	40
41	841.35011	.35011	0	874.89854	.89857	3	41
42	840.89544	.89543	-1	875.25100	.25101	1	42
43	840.43958	.43924	-34 A	875.60218	.60221	3	43
44	839.98254	.98255	1	875.95209	.95212	3	44
45	839.52432	.52429	-3	876.30072	.30074	2	45
46	839.06491	.06491	0	876.64807	.64803	-4	46
47	838.60431	.60432	1	876.99413	.99413	0	47
48	838.14254	.14253	1	877.33891	.33892	1	48
49	837.67957	.67954	-3	877.68240	.68237	-3	49
50	837.21543	.21545	2	878.02460	.02460	0	50
51	836.75010	.75011	1	878.36551	.36547	-4	51
52	836.28358	.28358	-0	878.70512	.70507	-5	52
53	835.81588	.81646	-58 A	879.04344	.04344	0	53
54	835.34700	.34696	-4	879.38046	.38049	3	54
55	834.87693	.87686	-7	879.71618	.71616	-2	55
56	834.40568	.40573	5	880.05060	.05056	-4	56
57	833.93324	.93325	1	880.38371	.38368	-3	57
58	833.45962	.45965	3	880.71551	.71550	-1	58
59	832.98481	.98479	-2	881.04601	.04601	0	59
60	832.50882	.50875	-7	881.37519	.37522	3	60
61	832.03164	.03163	-1	881.70306	.70301	-5	61
62	831.55327	.55327	-0	882.02961	.02960	-1	62
63	831.07372	.07379	7	882.35485	.35486	1	63
64	830.59299	.59287	-12	882.67876	.67873	-3	64
65	830.11106	.11078	-28 A	883.00134	.00134	0	65
66	829.62795	.62803	8	883.32260	.32260	0	66
67	829.14365	.14355	-10	883.64254	.64252	-2	67
68	828.65816	.65822	6	883.96114	.96121	7	68
69	828.17149	.17146	-3	884.27840	.27848	8	69
70	827.68363	.68338	-25 A	884.59433	.59433	0	70
71	827.19457	.19460	3	884.90892	.90888	-4	71
72	826.70433	.70438	5	-	-	-	72

wave numbers of Wells *et al.*¹ The spectrum over the ν_1 region is shown in Fig. 1. The molecular constants of $^{16}\text{O}^{12}\text{C}^{32}\text{S}$ derived from the unconstrained fit of the ν_1 band are presented in Table II. The values of the molecular constants are in good agreement with the values cited by Wells *et al.*,¹ and by Sattler *et al.*¹⁰ However, our standard deviation of ν_{BC} is smaller than the literature value.

B. ν_2 Band of $^{12}\text{C}^{16}\text{O}_2$

The partial pressure of CO_2 in the sample cell was uncertain, because CO_2 originated in the sample. However, the partial pressure was estimated to be ~ 0.05 Torr.

The observed wave numbers were fitted to a fourth-order polynomial, and the results are compiled in Table III. The standard deviation of the fit was $\sim 3.7 \times 10^{-5} \text{ cm}^{-1}$. The accuracy of the line positions is now an order of magnitude higher than in our previous work.³ Table II reveals the derived molecular constants of $^{12}\text{C}^{16}\text{O}_2$ compared with the corresponding literature values.¹¹⁻¹³

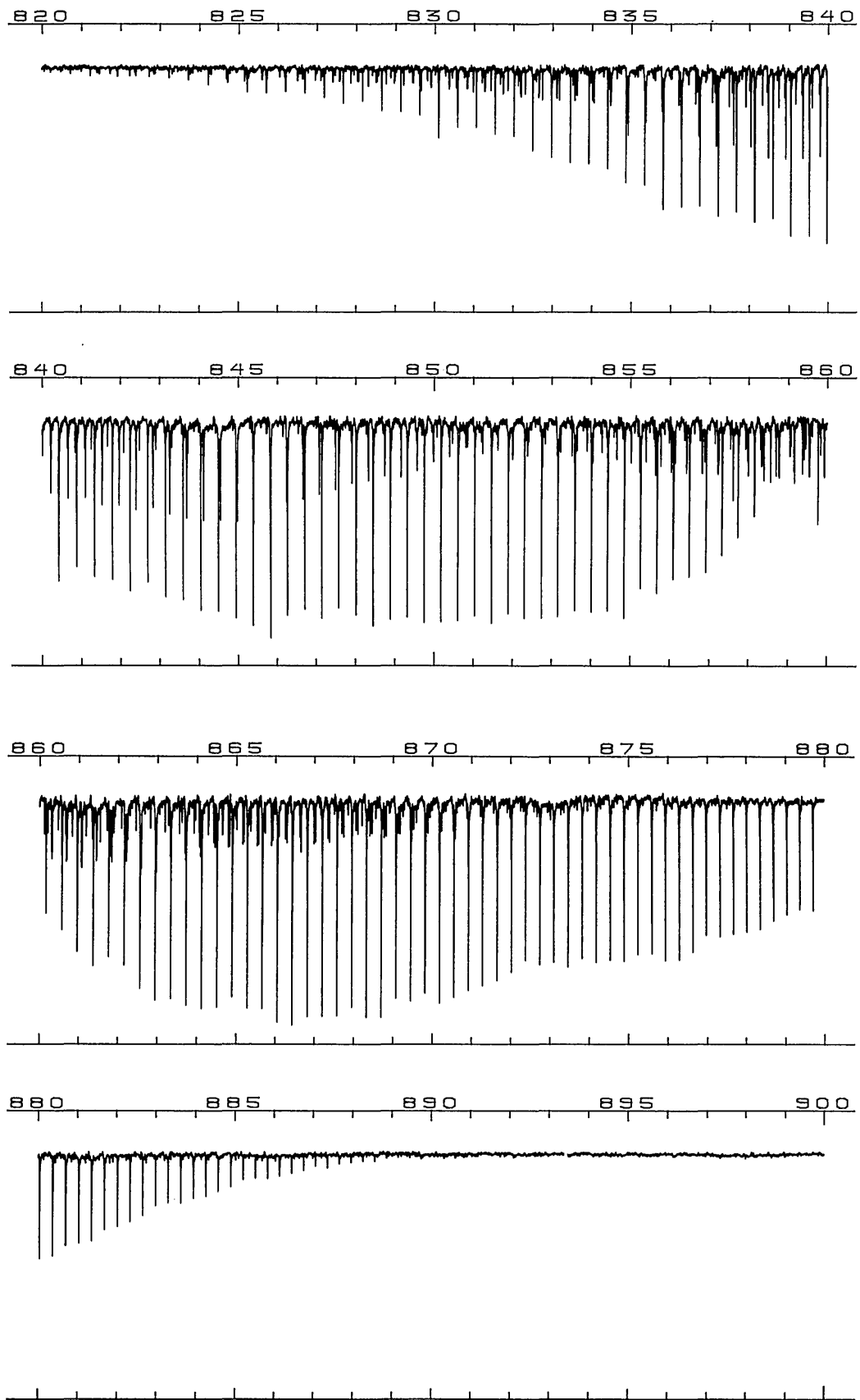


Fig. 1. Apodized spectrum of OCS over the ν_1 region with a resolution of $\sim 0.006 \text{ cm}^{-1}$. Absorption path length is 1 m, pressure is 0.30 Torr. The strongest lines are our ν_1 standard lines.

Table II. Results From the Analysis of the Fundamentals $01^1_0 \leftarrow 00^0_0$ of $^{12}\text{C}^{16}\text{O}_2$ and $10^0_0 \leftarrow 00^0_0$ of $^{16}\text{O}^{12}\text{C}^{32}\text{S}$

BAND PARAMETERS (cm^{-1})	$^{12}\text{C}^{16}\text{O}_2$ ($01^1_0 + 00^0_0$)			$^{16}\text{O}^{12}\text{C}^{32}\text{S}$ ($10^0_0 + 00^0_0$)	
	P and R branches	Q branch	Literature	P and R branches	Literature**
ν_{BC}	667.379979(9)	667.379974(17)		858.966936(6)	858.96691(2) [1]
$B_{00^0_0}$	0.39021895(17)	0.39021895(17)*	0.390218936(24) [11] 0.39021895(8) [12]	0.20285673(10)	0.2028567549(18) [1] 0.2028567415(4) [10]
$D_{00^0_0} \times 10^6$	0.133391(34)	0.133391(34)*	0.1333728(36) [11] 0.133318(27) [12]	0.043431(14)	0.0434279(4) [1] 0.0434113(16) [10]
$B_{01^1c_0}$	0.39063877(17)		0.39063942(25) [13]		
$B_{01^1d_0}$		0.39125439(20)	0.3912548(1) [12]		
$D_{01^1c_0} \times 10^6$	0.135332(34)		0.135353(58) [13]		
$D_{01^1d_0} \times 10^6$		0.136096(41)	0.13602(3) [12]		
$B_{10^0_0}$				0.20225177(10)	0.202251861(7) [1]
$D_{10^0_0} \times 10^6$				0.044332(14)	0.044360(7) [1]
Number of lines	64	29		136	
Std. dev. $\times 10^5$	3.7	4.6		3.6	

* Constrained (this work)

** To convert from frequency units to wavenumber units are used 299792458 m/s for the speed of light.

The error limits are standard deviations in the units of the last digits given.

The constants H have no significant values, constrained to zero.

Table III. Observed and Calculated Wave Numbers of the Fundamental $01^1_0 \leftarrow 00^0_0$ of $^{12}\text{C}^{16}\text{O}_2$ (A = Blended, B = Unresolved)

$01^1_0 \leftarrow 00^0_0$											
J	P(J) CALC.	OBS	O-C	R(J) CALC.	OBS	O-C	Q(J) CALC.	OBS	O-C	J	
0	-	-	-	668.16126	.16125	-1	-	-	-	0	
2	665.81995	.81990	-5	669.72632	.72631	-1	667.38619	.38620	1	2	
4	664.26330	.26332	2	671.29470	.29475	5	667.40069	.40062	-7	4	
6	662.71007	.71003	-4	672.86638	.86644	6	667.42347	.42355	8	6	
8	661.16027	.16028	1	674.44132	.44136	4	667.45453	.45452	-1	8	
10	659.61393	.61392	-1	676.01950	.01952	2	667.49387	.49391	4	10	
12	658.07106	.07108	2	677.60089	.60089	0	667.54148	.54143	-5	12	
14	656.53170	.53176	6	679.18546	.18544	-2	667.59735	.59737	2	14	
16	654.99587	.99589	2	680.77317	.77314	-3	667.66148	.66141	-7	16	
18	653.46358	.46356	-2	682.36399	.36399	0	667.73387	.73390	3	18	
20	651.93484	.93485	1	683.95790	.95790	0	667.81449	.81445	-4	20	
22	650.40969	.40968	-1	685.55486	.55483	-3	667.90335	.90340	5	22	
24	648.88814	.88818	4	687.15483	.15484	1	668.00043	.00015	-28 A	24	
26	647.37021	.37024	3	688.75778	.75770	-8	668.10570	.10570	0	26	
28	645.85591	.85591	0	690.36368	.36364	-4	668.21918	.21914	-4	28	
30	644.34526	.34529	3	691.97248	.97247	-1	668.34083	.34086	3	30	
32	642.83827	.83827	0	693.58416	.58409	-7	668.47066	.47070	4	32	
34	641.33496	.33492	-4	695.19866	.19867	1	668.60863	.60858	-5	34	
36	639.83534	.83531	-3	696.81597	.81598	1	668.75473	.75471	-7	36	
38	638.33943	.33942	-1	698.43603	.43598	-5	668.90894	.90901	2	38	
40	636.84723	.84725	2	700.05880	.05881	1	669.07125	.07126	1	40	
42	635.35876	.35873	-3	701.68425	.68424	-1	669.24162	.24154	-8	42	
44	633.87403	.87400	-3	703.31234	.31237	3	669.42005	.42004	-1	44	
46	632.39304	.39303	-1	704.94301	.94305	4	669.60651	.60650	-1	46	
48	630.91582	.91585	3	706.57624	.57629	5	669.80098	.80104	6	48	
50	629.44235	.44237	2	708.21197	.21202	5	670.00342	.00347	5	50	
52	627.97266	.97265	-1	709.85016	.85020	4	670.21382	.21380	-2	52	
54	626.50675	.50672	-3	711.49076	.49082	6	670.43214	.43215	1	54	
56	625.04463	.04453	-10	713.13374	.13375	1	670.65837	.65831	-6	56	
58	623.58629	.58639	10	714.77903	.77897	-6	670.89247	-	- B	58	
60	622.13176	.13179	3	716.42661	.42658	-3	671.13440	.13437	-3	60	
62	-	-	-	718.07641	.07644	3	671.38415	.38419	4	62	
64	-	-	-	719.72838	.72831	-7	-	-	-	64	
66	-	-	-	721.38249	.38249	0	-	-	-	66	

Table IV. Observed and Calculated¹⁴ Wave Numbers of the Pure Rotational Lines of H₂¹⁶O Between 500 and 720 cm⁻¹.

J'(K' _a ,K' _c)-J''(K'' _a ,K'' _c)	OBS	CALC	(O-C)×10 ⁵	J'(K' _a ,K' _c)-J''(K'' _a ,K'' _c)	OBS	CALC	(O-C)×10 ⁵
11(10, 2)-10(9, 1)	501.57203A	.5785	-647	10(6, 5)- 9(3, 6)	592.05415	.0546	-45
11(10, 1)-10(9, 2)				8(6, 2)- 7(3, 5)	594.94780	.9491	-130
10(4, 7)- 9(1, 8)	502.25802	.2561	+192	12(4, 9)-11(1, 10)	600.10368	.1042	-52
13(5, 8)-12(4, 9)	504.38306	.3877	-464	11(6, 6)-10(3, 7)	604.44853	.4487	-17
7(5, 2)- 6(2, 5)	506.92483A	.9252	-37	7(5, 3)- 6(0, 6)	612.95023	.9511	-87
12(9, 4)-11(8, 3)	510.42930A	.4204	+890	9(4, 5)- 8(1, 8)	616.07278	.0734	-62
12(9, 3)-11(8, 4)		.4248	+450	12(6, 7)-11(3, 8)	620.57733	.5784	-107
12(4, 8)-11(3, 9)	510.58403	.5852	-117	9(6, 3)- 8(3, 6)	625.26726	.2684	-114
11(11, 0)-10(10, 1)	514.30482	-		13(5, 9)-12(2, 10)	626.32242	.3247	-228
11(11, 1)-10(10, 0)		-		12(2, 10)-11(1, 11)	633.08992	.0902	-28
13(8, 5)-12(7, 6)	515.06211	.0641	-199	12(3, 10)-11(0, 11)	635.39701	.3982	-119
10(5, 6)- 9(2, 7)	516.79775A	.7973	+45	7(7, 1)- 6(4, 2)	637.03392	.0332	+72
10(2, 8)- 9(1, 9)	517.75912	.7588	+32	7(7, 0)- 6(4, 3)	638.08957	.0887	+87
11(3, 8)-10(2, 9)	519.58952	.5886	+92	13(3, 10)-12(2, 11)	639.97230	.9721	+20
10(3, 8)- 9(0, 9)	525.96024A	.9604	-16	10(5, 5)- 9(2, 8)	644.32015	.3202	-5
12(10, 3)-11(9, 2)	526.34358	.3406	+298	13(4, 10)-12(1, 11)	651.58024	.5818	-156
12(10, 2)-11(9, 3)		.3407	+288	10(6, 4)- 9(3, 7)	659.23058	.2310	-42
13(9, 5)-12(8, 4)	535.27178A	-		8(7, 2)- 7(4, 3)	659.45309	.4534	-31
13(9, 4)-12(8, 5)		-		8(7, 1)- 7(4, 4)	662.94680	.9473	-50
6(6, 1)- 5(3, 2)	536.24615	.2451	+105	8(5, 4)- 7(0, 7)	668.92369	.9243	-61
6(6, 0)- 5(3, 3)	541.09037	.0893	+107	14(5, 10)-13(2, 11)	671.36010	-	
8(4, 4)- 7(1, 7)	545.29660	.2972	-60	9(7, 3)- 8(4, 4)	678.80798	.8088	-82
8(5, 3)- 7(2, 6)	546.30359	.3044	-81	9(7, 2)- 8(4, 5)	687.87946	.8806	-114
11(5, 7)-10(2, 8)	547.81661	.8164	+21	13(2, 11)-12(1, 12)	689.03703	.0388	-177
11(4, 8)-10(1, 9)	550.01159	.0114	+19	13(3, 11)-12(0, 12)	690.22009	.2228	-271
7(6, 2)- 6(3, 3)	554.64087	.6417	-83	10(7, 4)- 9(4, 5)	694.11012	.1111	-98
6(5, 2)- 5(0, 5)	563.25099	.2512	-21	10(4, 6)- 9(1, 9)	696.24299	.2437	-71
7(6, 1)- 6(3, 4)	567.21597	.2165	-53	14(3, 11)-13(2, 12)	697.05439	.0536	+79
8(6, 3)- 7(3, 4)	569.25512	.2564	-128	11(6, 5)-10(3, 8)	697.91815	.9173	+85
13(4, 9)-12(3, 10)	571.28643	.2894	-297	14(4, 11)-13(1, 12)	703.71295	.7142	-125
11(2, 9)-10(1, 10)	576.11444	.1144	+4	11(5, 6)-10(2, 9)	705.35115	.3617	-55
11(3, 9)-10(0, 10)	580.53641	.5371	-69	11(7, 5)-10(4, 6)		.3613	-15
12(3, 9)-11(2, 10)	580.73189	.7313	+59	8(6, 3)- 7(1, 6)	707.39737	.3980	-63
9(6, 4)- 8(3, 5)	581.08810	.0891	-100	10(7, 3)- 9(4, 6)	713.48385	.4853	-145
12(5, 8)-11(2, 9)	584.70877	.7094	-63	12(7, 6)-11(4, 7)	713.79165	.7933	-165
9(5, 4)- 8(2, 7)	591.69728	.6978	-52				

C. Pure Rotational Lines of H₂¹⁶O

As mentioned above, the main aim of this work was to transport the high accuracy of seven OCS lines to pure rotational lines of H₂O. The observed standard wave numbers of H₂¹⁶O between 500 and 720 cm⁻¹ are given in Table IV and compared with the values calculated by Kyrö.¹⁴

IV. Conclusion

Our standard deviations for the wave numbers were very small, typically ~3.6 × 10⁻⁵ cm⁻¹ (1.2 MHz), and the highest accuracy was achieved in the value of the band center ν_{BC} of ¹⁶O¹²C³²S shown in Table II. This value is ν_{BC} = 858.966936 ± 0.000006 cm⁻¹ gives |dν_{BC}|/ν_{BC} ≈ 7 × 10⁻⁹. This is close to the value |dc|/c ≈ 4 × 10⁻⁹, where the speed of light c = 299792458 ± 1.2 m/sec.

The very high accuracy of ν_{BC} is partly related to the very high linearity of the wave-number scale of the Fourier transform spectrometer. However, the absolute accuracy of the wave number is limited by the accuracies of the seven reference lines of OCS used for calibration. The absolute accuracy of these seven OCS lines determines the absolute uncertainty of our wave numbers to a value of ~4.5 × 10⁻⁵ cm⁻¹ (1.5 MHz).

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References

1. J. S. Wells, F. R. Petersen, A. G. Maki, and D. J. Sukle, *Appl. Opt.* **20**, 1676 (1981).
2. J. Kauppinen and E. Kyrö, *J. Mol. Spectrosc.* **71**, 15 (1978); **84**, 405 (1980).
3. R. Paso, J. Kauppinen, and R. Anttila, *J. Mol. Spectrosc.* **79**, 236 (1980).
4. J.-P. Monchalain, M. J. Kelly, J. E. Thomas, N. A. Kurnit, and A. Javan, *J. Mol. Spectrosc.* **64**, 491 (1977).
5. C. Freed, L. C. Bradley, and R. G. O'Donnell, *IEEE J. Quantum Electron.* **QE-16**, 1195 (1980).
6. J. Kauppinen, *Appl. Opt.* **14**, 1987 (1975).
7. J. Kauppinen, *Appl. Opt.* **18**, 1788 (1979).
8. J. Kauppinen, *Acta Univ. Oulu A38*, (1975).
9. J. Kauppinen and V. -M. Horneman, "Research Reports in Optics," in *Proceedings, Symposium of Optics*, 23 Nov. 1981, Helsinki U. Technology, Finland.
10. J. P. Sattler, T. L. Worchesky, A. G. Maki, and W. J. Lafferty, *J. Mol. Spectrosc.* **90**, 460 (1981).
11. A. S. Pine and G. Guelachvili, *J. Mol. Spectrosc.* **79**, 84 (1980).
12. D. Bailly, R. Farrenq, G. Guelachvili, and C. Rossetti, *J. Mol. Spectrosc.* **90**, 74 (1981).
13. G. Guelachvili, *J. Mol. Spectrosc.* **79**, 72 (1980).
14. E. Kyrö, *J. Mol. Spectrosc.* **88**, 167 (1981).